THEORETICAL CHEMISTRY INSTITUTE

THE UNIVERSITY OF WISCONSIN

APPROXIMATE PERTURBATION TREATMENT OF H_2^+

by

William D. Lyon, William A. Sanders

and

Joseph O. Hirschfelder

WIS-TCI-142 13 December 1965

MADISON, WISCONSIN

APPROXIMATE PERTURBATION TREATMENT OF H_2^+ *

by

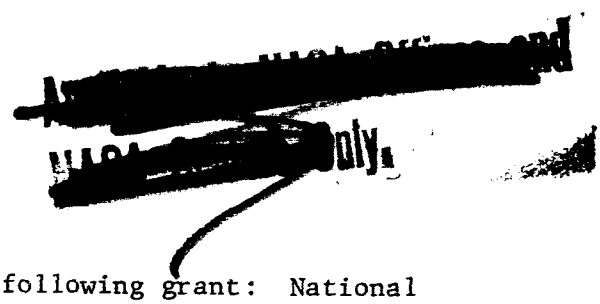
William D. Lyon, William A. Sanders

and

Joseph O. Hirschfelder

ABSTRACT

A procedure for approximating a correct perturbation of two interacting atoms in the region of overlap was used to calculate the energy of H_2^+. As a result of symmetry considerations, the results were not promising.



* This research was supported by the following grant: National Aeronautics and Space Administration Grant NsG-275-62(4180).

It is extremely difficult to use perturbation theory to calculate interatomic forces when the charge distributions of the two atoms overlap. Thus, we tried a simplified procedure to calculate the energy of H_2^+. Unfortunately, the results were not promising. Our failure was due to the fact that our zeroth order wavefunction did not have the same symmetry as the exact wavefunction which we were seeking to approximate.

In a recent paper of Lyon, Matcha, Sanders, Meath, and Hirschfelder[1], the energy of the H_2^+ ground state was approximated correctly by a perturbation procedure starting with the zeroth order wavefunction

$$\psi_o = N(a_o + b_o) ,$$

where a_o and b_o are 1s hydrogen orbitals $\pi^{-\frac{1}{2}} \exp(-r)$ centered on nucleus "a" and "b" respectively. A first order wavefunction $\psi_o^{(1)}$ was obtained together with the first, second and third order perturbation energies: $\epsilon_o^{(1)}$, $\epsilon_o^{(2)}$, and $\epsilon_o^{(3)}$. In addition, $E_o(1)$, the expectation value of the Hamiltonian with respect to the wavefunction $\psi_o + \psi_o^{(1)}$ was calculated.

There is another perturbation treatment of H_2^+ which is not nearly so accurate. Here a_o is taken as the zeroth order wavefunction so that the perturbation corresponds to the

polarization[2] due to the nucleus at b . The first order wavefunction is $a_o^{(1)}$ and the zeroth, first, and second order energies are denoted by ϵ_a , $\epsilon_a^{(1)}$, and $\epsilon_a^{(2)}$. The expectation value of the Hamiltonian with respect to the wave function $a_o + C\, a_o^{(1)}$ is denoted by $E_a^{(1)}{}_C$. The value of the constant C is varied so as to give the minimum energy when $C = C(\text{min})$.

We tried to improve the polarized hydrogen atom treatment by using the zeroth order wavefunction ψ_o but approximating the first order wave function by $\tilde{\psi}^{(1)} = N\left[a_o^{(1)} + b_o^{(1)}\right]$, where $b_o^{(1)}$ has the same functional form as $a_o^{(1)}$ except that it is centered on b . Corresponding to $\tilde{\psi}^{(1)}$, the approximate second order energy is

$$\tilde{\epsilon}^{(2)} = \left(1 + \langle b_o | a_o \rangle\right)^{-1}\left[\epsilon_a^{(2)} + \langle b_o | H - H_a | a_o^{(1)} \rangle - \epsilon_a^{(1)} \langle b_o | a_o^{(1)} \rangle\right].$$

We calculated $\tilde{E}^{(1)}{}_C$, the expectation value of the Hamiltonian with respect to $\psi_o + c\,\tilde{\psi}^{(1)}$ and varied the value of C so as to give the minimum energy when $C = C(\text{min})$.

Robinson[3] suggested a somewhat cruder approximation: Replace $\epsilon_o^{(2)}$ by $\epsilon_a^{(2)} = \langle a_o^{(1)} | H - H_a | a_o \rangle$, where H_a is the Hamiltonian of a hydrogen atom centered at a . Thus, he obtained the approximate energy through second order

$$E_R = \epsilon_o + \epsilon_o^{(1)} + \epsilon_a^{(2)} .$$

His results are surprisingly accurate; we don't know why!

The calculated values for the energy of H_2^+ are given in Table 1. The exact energy is taken from the very, very accurate variational treatment of Peek[4].

Our new calculations of $\epsilon_o + \epsilon_o^{(1)} + \tilde{\epsilon}^{(2)}$, $\tilde{E}^{(1)}_{c=1}$, and $\tilde{E}^{(1)}_{c(min)}$ are not as accurate as we had hoped. We think that the explanation must be due to symmetry considerations rather similar to those which Robinson discussed in connection with an idealization of the diatomic hydrogen ion. Robinson showed[3], using a delta-function model for the electronic potential energy of H_2^+ treated as a polarized hydrogen atom, that the perturbation sequence does not converge at large values of internuclear separation, R . This result is reasonable since the series solution cannot decide whether to converge to the gerade or ungerade state of the model. If this result can be extended to the actual physical problem, it would appear that energies generated by the sequence (a_o , $a_o^{(1)}$, ...) could not converge to the correct H_2^+ energies.

We would like to thank Mrs. Carol Constable for computational assistance. All calculations were done at the University of Wisconsin Computing Center on a CDC 1604 computer.

TABLE I

Energy of H_2^+ Ground State Calculated by Perturbation Procedures. Distances and energies are given in atomic units. The energy of nuclear-nuclear interaction is omitted. The values in parentheses are c(min).

R	$-(\epsilon_a+\epsilon_a^{(1)}+\epsilon_a^{(2)})$	$-(\epsilon_o+\epsilon_o^{(1)}+\tilde{\epsilon}^{(2)})$	$-(\epsilon_o+\epsilon_o^{(1)}+\epsilon_a^{(2)})$	$-E_a^{(1)}{}_{c=1}$	$-E_a^{(1)}{}_{c(min)}$
0.2	1.939101	1.914204	1.944548	1.745030	1.789172
0.6	1.675558	1.601763	1.707971	1.562259	1.586395
1.0	1.428638	1.357362	1.487675	1.385761	1.392043
1.5	1.200642	1.166797	1.278635	1.201140	1.201142
2.0	1.042781	1.044839	1.124025	1.055991	1.058579
2.5	0.932985	0.956048	1.007247	0.946031	0.951029
3.0	0.855714	0.886504	0.918102	0.865051	0.869808
4.0	0.759355	0.785385	0.796640	0.762694	0.764348
5.0	0.704038	0.719472	0.723296	0.705046	0.705370
6.0	0.668588	0.676405	0.677663	0.668890	0.668946
7.0	0.643870	0.647503	0.647906	0.643968	0.643978
8.0	0.625583	0.627187	0.627312	0.625619	0.625620
9.0	0.611470	0.612155	0.612194	0.611484	0.611485
10.0	0.600233	0.600520	0.600531	0.600240	0.600240
Reference Numbers	2		3		

	$-\tilde{E}(1)_{c=1}$	$-\tilde{E}(1)_{c(min)}$		$-E_o(1)$	$-E_{exact}$
(0.67070)	1.748676	1.792491	(0.67057)	1.744361	1.928620
(0.71386)	1.582507	1.605815	(0.70927)	--	1.671485
(0.81623)	1.414802	1.421269	(0.79364)	1.401124	1.451786
(1.00421)	1.235017	1.235457	(0.91811)	--	1.248990
(1.22482)	1.095082	1.095082	(1.00091)	1.094290	1.102634
(1.42535)	0.989105	0.989109	(1.01581)	--	0.993824
(1.54862)	0.908109	0.908110	(1.00478)	0.909521	0.910896
(1.51071)	0.795378	0.795386	(1.03322)	0.795818	0.796085
(1.32521)	0.724262	0.724301	(1.10191)	0.724332	0.724420
(1.18529)	0.678573	0.678616	(1.14291)	0.678588	0.678636
(1.10579)	0.648418	0.648442	(1.14366)	--	0.648451
(1.06380)	0.627555	0.627564	(1.12018)	0.627559	0.627570
(1.04091)	0.612300	0.612303	(1.08984)	--	0.612307
(1.02789)	0.600576	0.600576	(1.06262)	0.600577	0.600579
				1	4

References

1. W. D. Lyon, R. L. Matcha, W. A. Sanders, W. J. Meath and J. O. Hirschfelder, J. Chem. Phys., 43, 1095 (1965).

2. A. Dalgarno and N. Lynn, Proc. Phys. Soc. (London), A70, 223 (1957); P. D. Robinson, Proc. Phys. Soc. (London), A71, 828 (1958).

3. P. D. Robinson, Proc. Phys. Soc. (London), A78, 537 (1961).

4. J. M. Peek, Sandia Corp. Research Report SC-RR-65-77 (1965).